



Action spectra of P25 TiO₂ and a visible light absorbing, carbon-modified titania in the photocatalytic degradation of stearic acid



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ABSTRACT

The photonic efficiencies of films of Evonik (formerly Degussa) P25 TiO₂ and carbon-modified TiO₂ Kronos VLP 7000 samples are reported as a function of excitation wavelength (300–430 nm; FWHM ~ 7.5 nm), i.e. the action spectra, for the degradation of stearic acid, a model organic for the photocatalytic destruction of solid surface organic pollutants. For each of these semiconductor photocatalysts, at 365 nm (FWHM = 18 nm), the dependence of the rate of degradation of stearic acid, upon the irradiance, I , is determined and the rate is found to be proportional to $I^{0.65}$ and $I^{0.82}$ for P25 and Kronos titania, respectively. Assuming this relationship holds at all wavelengths, the action spectra for two different semiconductor photocatalysts is modified by plotting, $(R_{SA}/I = \text{photonic efficiency}, \xi)$ vs. λ_{excit} . The shape of the modified action spectrum for P25 TiO₂ is consistent with that reported by others for other organic mineralisation reactions and correlates well with diffuse reflectance data for P25 TiO₂ (Kubelka–Munk plot), although there is some evidence that the active phase, in the photodegradation of stearic acid, is the anatase form present in P25. The unmodified and modified action spectra of the beige Kronos VLP 7000 TiO₂ compound exhibits little or no activity in the visible i.e. ($\lambda_{\text{excit}} > 400$ nm) and a peak at 350 nm. The Kronos powder contains a yellow/brown conjugated, extractable, organic sensitizer which has been identified by others as the species responsible for its reported photocatalytic visible light activity. But, irradiation of the Kronos powder film, with and without a stearic acid coating, in air, using UVA or visible light, bleaches rapidly (<60 min) most, if not all, of the little colour exhibited by the original Kronos powder. The photobleached form of the Kronos has a similar action spectrum to that of the unbleached form, which, in turn, appears very similar to that of P25 titania, at wavelengths >350 nm. It is proposed that the difference between the Kronos and P25 powder films at wavelengths <350 nm is due to a photodegradation-resistant, previously unidentified (but extractable using MeCN) UV-absorbing organic species in the former which screens the titania particles at these lower wavelengths. The implications of these observations are discussed briefly.

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1. Introduction

Most photocatalysis studies are carried out under broadband illumination, i.e. not using monochromatic light, which can make it difficult to calculate the efficiency of the photocatalyst and to gain an understanding of the mechanism of the process. Greater insight into the underlying photochemical process(es) can be obtained by determining the action spectrum of a photocatalyst, i.e. a plot of the photocatalytic rate or yield per unit number of photons as a function

of the wavelength or energy of irradiation. The ratio of the initial rate (example units: moles cm⁻² s⁻¹) to incident irradiance (example units: photons cm⁻² s⁻¹) is defined as the photonic efficiency of the system, ξ , if monochromatic light is used [1,2], and formal quantum efficiency, FQE, if polychromatic irradiation is used. Proof that a semiconductor photocatalyst is the light-absorbing species responsible for a photocatalytic reaction is often taken if the action spectrum of the photocatalyst and the absorption, or reflectance, spectrum of the semiconductor photocatalyst are similar [3,4]. For example, Fig. 1 illustrates the reported [3] action spectrum for the photocatalytic, oxidative mineralisation of acetic acid by Evonik P25 titania and the measured (in this work) diffuse reflectance spectrum of P25, where both sets of data have been normalised at 350 nm so as to effect a ready comparison of their spectral profiles.

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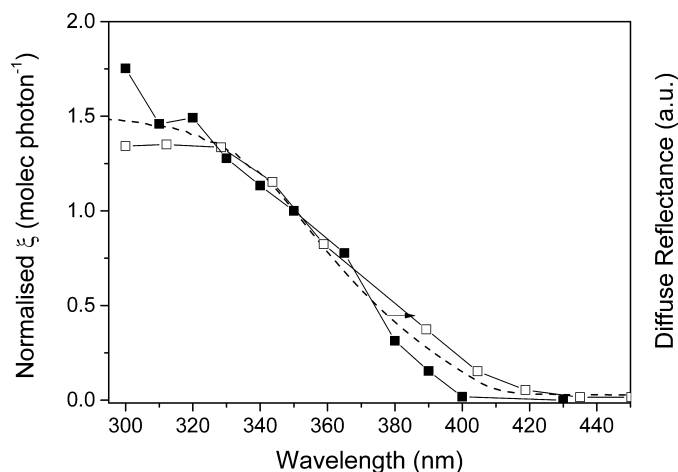


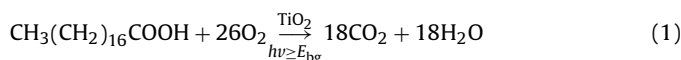
Fig. 1. Normalised photonic efficiency (ξ) or modified photonic efficiency (ξ') and diffuse reflectance spectrum (Kubelka–Munk function; broken line) of P25 titania film as a function of the peak wavelength of the excitation light, λ_{excit} . The normalised ξ or ξ' data are represented by solid lines with (\square) and (\blacksquare) data points and are for the photocatalytic oxidative degradation of acetic acid [3] (ξ) and stearic acid (ξ' , this work), respectively.

The similarity of the two spectra is striking and provides strong evidence that P25 is the light-absorbing species in the photodecomposition of the acetic acid. In contrast, Ohtani et al. [5] found that the rate of photobleaching of methylene blue by P25 titania exhibited a similar high rate of photobleaching when irradiated with either 665 nm light, where only the dye absorbs, or with 400 nm light, where the semiconductor absorbs. The former feature is due to a dye-sensitised (i.e. not semiconductor-sensitised) photobleaching process, whereas the latter is due to the desired semiconductor-sensitised, photocatalytic oxidative mineralisation process [5]. This classic experiment highlights the danger of using dyes as model pollutants, especially when assessing the visible light photocatalytic activity of a semiconductor. These authors rightly urge all researchers to run action spectra when studying new photocatalyst materials in order to minimise the likelihood of a photosensitised reaction being misinterpreted as an example of a rarer and more sought example of visible-light driven photocatalysis [5].

In semiconductor photocatalysis, interpreting an action spectrum is complicated by the fact that the rate of a photocatalytic process may not necessarily depend directly upon irradiance, I . For example, it is often found that rate is proportional to I , or $I^{1/2}$, at low, or high irradiance values, respectively, or proportional to I^θ , where $0.5 < \theta < 1$ for intermediate irradiance values. However, defining what constitutes low, high or intermediate irradiance conditions is difficult, since it depends upon many factors including: reactor design (reflectivity, illumination uniformity), the photocatalytic process under investigation and how strongly the light is absorbed by the semiconductor particles. Thus, a reported action spectrum may well be distorted, and so very different from the underlying absorption/reflectance spectrum of the semiconductor photocatalyst, if there is a significant variation (e.g. >100%) in the irradiance, I , as the wavelength is varied and a nonlinear dependence of the rate of the photocatalytic process upon I . One possible way to correct this distortion is to produce a modified action spectrum in which (rate/I^θ) is plotted as a function of excitation wavelength.

In this work, a film of stearic acid (octadecanoic acid) is used as the test pollutant, since it is one of the most common fatty acids in nature and is commonly used as a model compound to evaluate the degradation of solid organic pollutants on solid photocatalytic films [6–10]. Amongst its attractions as a model test pollutant of photocatalyst films is its high stability under UV irradiation, in the absence of an underlying, effective photocatalyst film, and

that the kinetics of its removal typically follows simple zero-order kinetics. The latter point is significant in that the initial concentration/thickness of the stearic acid is not a critical factor in the evaluation of film photocatalytic activity, except under low (sub-monolayer) coverage conditions, which are not usually employed as their quantitative analysis can pose a challenge. Another attractive feature of stearic acid is that, for transparent samples, such as titania films on glass, its degradation can be easily monitored via infrared spectroscopy, following the disappearance of C–H stretching modes from CH_2 and CH_3 groups in the region $2700\text{--}3000\text{ cm}^{-1}$ [6]. The overall photocatalytic mineralisation of stearic acid can be summarised as follows:



Of the titania films tested in this work, one comprised particles of Evonik (formerly Degussa) P25 TiO_2 , a white powder, which is a renowned, highly active reference semiconductor photocatalyst when irradiated with UV light (i.e. below ca. 400 nm). Given titania's poor overlap with the solar spectrum, in recent years strenuous efforts have been devoted to extending its range of light absorption into the visible range for outdoor applications, especially by doping it with non-metals, such as nitrogen or carbon [11–15]. Thus, in this work, films of the commercial beige-coloured TiO_2 -based Kronos VLP 7000 powder product were also examined, as it is reported to be a highly-efficient visible-active photocatalyst for a wide range of indoor and outdoor photo-degradation applications [16,17]. Interestingly, it has been reported [17] that this material is not carbon-doped TiO_2 , which would involve the presence of intragap localised energy states in the semiconductor, but rather a carbon-modified sample, in which the thermally produced carbon compound, an arylcarboxylate, acts as a visible light photosensitiser for the destruction of organic test pollutants, such as 4-chlorophenol.

This paper investigates the action spectra of films of the UV-active and ubiquitous P25 TiO_2 and the reported visible-light active photocatalyst, Kronos VLP 7000, in the photocatalytic mineralisation of stearic acid, as measured using FT-IR spectroscopy.

2. Experimental

2.1. Materials

Evonik P25 TiO_2 powder comprises particles which are a mixture of mainly anatase and rutile phases (typically 70–80% anatase), with a BET surface of ca. $50\text{ m}^2\text{ g}^{-1}$ [18]. The C-modified Kronos VLP 7000 C-modified TiO_2 powder, has a titania content of 95%, crystallite size of ca. 15 nm and BET surface ca. $250\text{ m}^2\text{ g}^{-1}$. XRD reveals the titania in the Kronos powder to be in its anatase crystalline form.

2.2. Film preparation

Thin films of both products were deposited by dip-coating borosilicate microscope glass slides ($75 \times 25 \times 1\text{ mm}$, VWR International) into 5 wt% aqueous dispersions of the powders. In this work the slides were immersed for 20 s and then withdrawn at 300 mm min^{-1} . The films were then dried at 30°C for 30 min and then at 100°C for 1 h. Finally the slide was washed with water and left to dry in air. This process was repeated three times on each slide to build up the deposited photocatalyst powder film layer, following the optimum conditions for deposition reported elsewhere [19]. At the end of this exercise, and before the subsequent deposition of a layer of stearic acid, the TiO_2 coating on the back of the slide was removed by wiping with cotton wool soaked in a 5 M aqueous NaOH solution [20]. The average masses of the P25 TiO_2 and Kronos C-modified TiO_2 films created using this procedure were 0.12

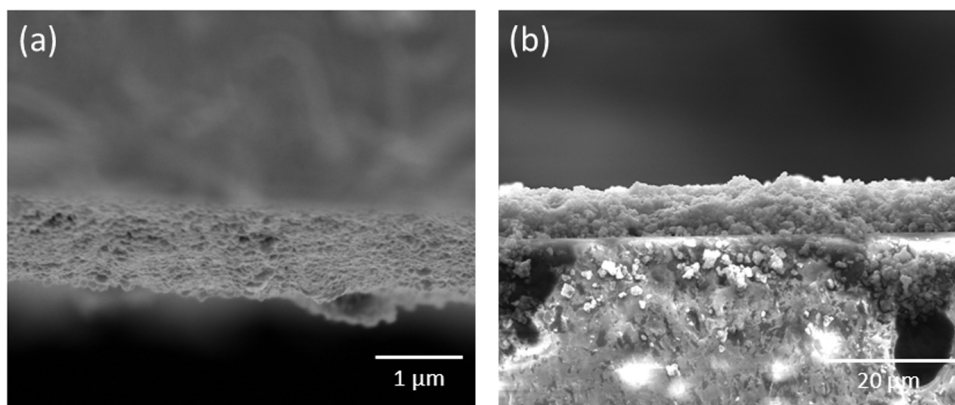


Fig. 2. Side-view SEM images obtained from (a) P25 ($\times 20,000$) and (b) Kronos ($\times 4000$) films; the average thicknesses measured from several SEM images were ca. 1 and 7.5 μm , respectively.

and 0.35 mg cm^{-2} , respectively. The average thicknesses of typical P25 and Kronos films were determined by SEM, see Fig. 2(a) and (b), as ca. 1 and 7.5 μm , respectively. Although, in terms of mass, there was 3 times more Kronos titania powder on the slides than P25, the significant difference in thickness, suggests that the former forms more voluminous, i.e. more porous, films, which is not too surprising given that the specific surface area of the powder is ca. 5 times that of P25. Following the preparation of the two different titania on microscope slide samples, a thin layer of stearic acid (SA) was then deposited on each and every sample, also by dip-coating, using a 0.1 M stearic acid solution in chloroform as the coating solution, with an immersion time of 1 s and a withdrawal speed of 1000 mm min^{-1} . The stearic acid deposited on the back (i.e. non- TiO_2 coated) of the slide was thoroughly cleaned using a cotton wool bud soaked in high purity chloroform. All films were then stored in the dark prior to use.

2.3. Powder and film characterisation

Diffuse reflectance UV–Vis spectra were obtained from the sample powders using a Perkin-Elmer Lambda 35 spectrometer (scan speed 30 nm min^{-1}) equipped with a Labsphere RSA-PE-20 Reflectance accessory. Further reflectance studies of the films were carried out using a Konica Minolta CM-2500D spectrophotometer. Scanning electron microscopy (SEM) images were obtained using Jeol 6500 FEG and FEI Quanta 650 FEG environmental (ESEM) microscopes.

2.4. Irradiation sources and irradiance measurement

A Xe KiloArc lamp (OBB Corp.), fitted with a monochromator (slit widths, 2 mm), was used to select bands of light (typically, FWHM $\sim 7.5 \text{ nm}$) for irradiating the photocatalyst films under test at different wavelengths, spanning the range 300–430 nm. The excitation wavelengths, λ_{excit} , selected were typically spaced 10 nm apart in order to avoid significant overlap. It was noted that the grating in the monochromator allowed transmission of emission secondary bands at half wavelength, which fell into the UVC region. Interestingly, these secondary bands, albeit weaker than the primary, allowed the UV-only absorbing P25 photocatalyst films to degrade the surface coating of stearic acid when irradiated with light $\geq 400 \text{ nm}$. In order to avoid this apparent (but not real) visible light activity for P25, and possibly Kronos, titania, all action spectra data recorded using light in the region 390–430 nm utilised a plain borosilicate glass slide filter (cut-off ca. 320 nm) to remove any artefact UVC component in the incident light. The emission spectra of the irradiation bands used in the action studies, together

with a plot of the corresponding irradiances as a function of wavelength, are shown in Fig. 3. Some additional irradiation experiments at 365 nm (FWHM 18 nm), in which the UV irradiance was varied and the rate of stearic acid degradation determined, were carried out using a blacklight-blue (BLB) UVA lamp ($2 \times 8 \text{ W}$). All light emission spectra were recorded using a high-performance, calibrated UV–Vis OL 756 spectroradiometer (Gooch & Housego), equipped with an integrating sphere.

2.5. The photocatalytic destruction of stearic acid

Details of how the stearic acid was deposited on the photocatalyst-coated microscope slides are given above and, once prepared, each film was irradiated with light, either from the Xe KiloArc/monochromator system or the 365 nm (FWHM 18 nm) BLB's as described above. In this work the photocatalytic degradation of stearic acid was monitored by FT-IR absorption spectroscopy, using a Perkin Elmer, Spectrum one, FTIR spectrophotometer. Fig. 4(a) illustrates a set of typical FT-IR spectra recorded for the destruction of stearic acid on a P25 titania film, over the range $2700\text{--}3000 \text{ cm}^{-1}$, when irradiated with 365 nm light from the Xe KiloArc/monochromator system (irradiance $= 0.56 \text{ mW cm}^{-2}$). For each recorded FT-IR spectrum the integrated area, A_{int} , under the SA absorption peaks was calculated and a resulting plot of the integrated area (units: cm^{-1})

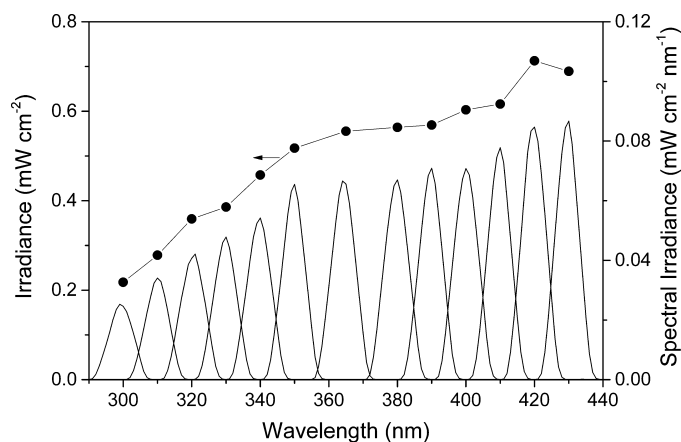


Fig. 3. Plots of emission spectra (i.e. spectral irradiance (units: $\text{mW cm}^{-2} \text{ nm}^{-1}$) vs. λ_{excit}) and corresponding irradiances (obtained by integrating the area under the peaks in the emission spectra) vs. λ_{excit} (●). The data were generated using a 1 kW Xe arc lamp coupled to a monochromator, which was the same system used to generate the action spectra of the Evonik P25 and Kronos TiO_2 films for the photocatalytic destruction of stearic acid.

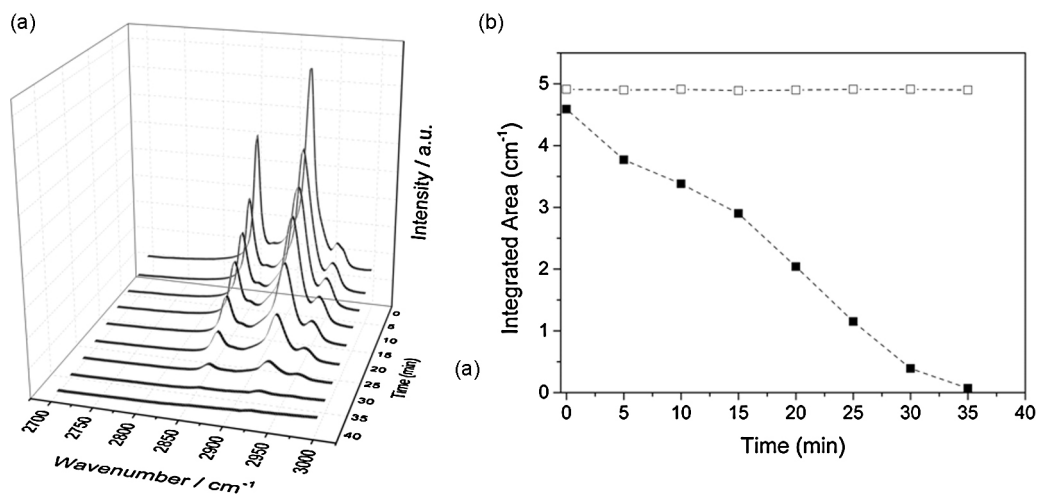


Fig. 4. (a) Some of the recorded FT-IR spectra of a typical stearic acid film deposited on P25 TiO₂ film as a function of irradiation time, t , using 365 nm (FWHM ~ 7.5 nm; irradiance: 0.56 mW cm^{-2}) and (b) corresponding integrated areas (under each of the spectra in (a)) as a function of t (■). The open square data (□) correspond to the stearic acid decay curve recorded for a film deposited on plain glass. From the recorded decay profile the initial rate of stearic acid decay (units: $\text{cm}^{-1} \text{ min}^{-1}$) was determined over the first 20% of the decay (in this case: $0.13 \text{ cm}^{-1} \text{ min}^{-1}$, from which a value for $\xi = 0.021$ molecules/incident photon was derived).

vs. irradiation time generated, see Fig. 4(b). Other work [6] shows that A_{int} value of 1 cm^{-1} is equivalent to 9.7×10^{15} molecules of stearic acid cm^{-2} . From the initial (first 20%) decay of the SA, plotted in the form A_{int} vs. irradiation time, an initial rate for the destruction of SA can be calculated, R_{SA} (units: molecules of SA $\text{cm}^2 \text{ s}^{-1}$). From the data illustrated in Fig. 4(b), the value for ξ ($=R_{\text{SA}}/I$) of 0.021 molecules/incident photon was derived.

3. Results and discussion

The visible light absorption of the commercial C-modified titania powder, Kronos VLP 7000 TiO₂, in the visible range is evidenced not only by its weak beige colour, but more quantitatively by a long tail extending beyond 400 nm in the corresponding Kubelka–Munk (K–M) plot of its diffuse reflectance spectrum, as illustrated in Fig. 5. In contrast, the K–M plot for the white P25 TiO₂ powder shows no such tail in the visible (see Fig. 5) and, consequently, is unlikely to yield any discernible photocatalytic activity when irradiated with visible light ($>400 \text{ nm}$), i.e. it can be considered as a UV-active only photocatalyst material.

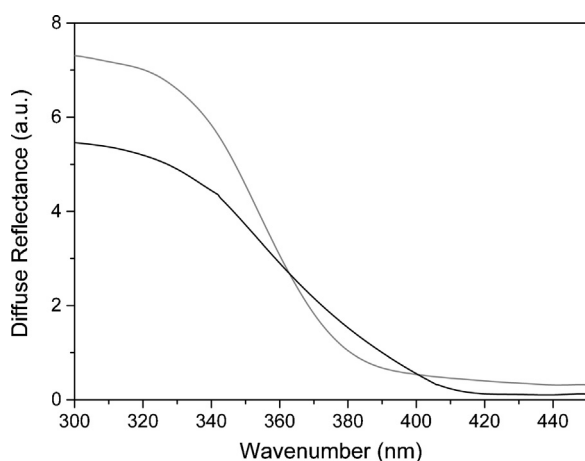


Fig. 5. Diffuse reflectance spectra of P25 TiO₂ (black line) and Kronos C-modified TiO₂ (grey line) powders.

3.1. Action spectra

The two photocatalytic film types, comprising P25 titania and Kronos VLP 7000 TiO₂ powders, respectively, were tested for photocatalytic activity as a function of irradiation wavelength, using a film of stearic acid (SA) as the test pollutant and a kW Xe arc/monochromator system to provide light of different wavelengths, λ_{excit} . Using this system the values of R_{SA} were determined as a function of wavelength, λ_{excit} , the irradiance band peak wavelength, for both P25 and Kronos VLP 7000 TiO₂ films. The spectral irradiance (units: $\text{mW cm}^{-2} \text{ nm}^{-1}$) data in Fig. 3 allow the irradiances at these different values of λ_{excit} to be calculated both in mW cm^{-2} and, more importantly here, number of photons $\text{cm}^{-2} \text{ s}^{-1}$, i.e. I . Thus, for each peak wavelength, λ_{excit} , of excitation irradiation used, the ratio of the measured associated parameters R_{SA}/I ($=\xi$) was calculated for both P25 and Kronos powder film samples. A plot of ξ vs. λ_{excit} for the two film types is illustrated in Fig. 6 and are the action spectra of the P25 titania and Kronos VLP 7000 TiO₂ powder films, although not equivalent to a plot of quantum

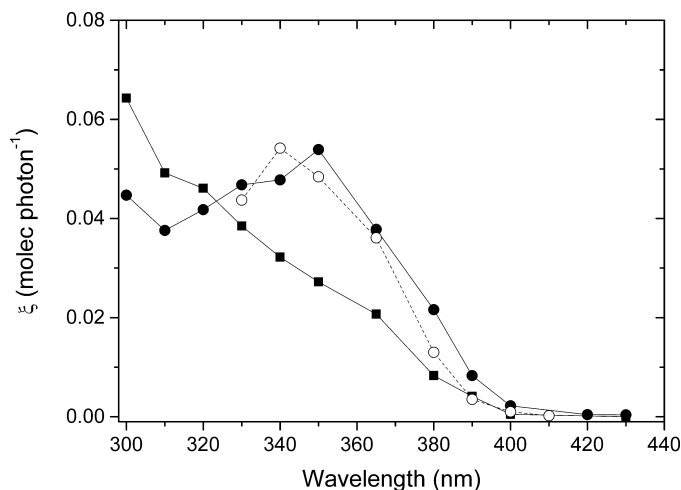


Fig. 6. Action spectra (i.e. plots of ξ vs. λ_{excit}) of P25 TiO₂ (■) and C-modified (Kronos) TiO₂ (●) films evaluated during photo-degradation of stearic acid. The open circle data (○) corresponds to the action spectra of UVA-bleached Kronos TiO₂ films. Each point illustrated is the average of three decay profiles for that value of λ_{excit} for which the error was typically $<10\%$.

yield as a function of irradiation wavelength. Unfortunately, the measurement of quantum yields is notoriously difficult to make in heterogeneous photocatalysis and most research groups report, at best, photonic efficiency or FQE values, which make the gross assumption that all incident light is absorbed [2]. As a result, for any incident wavelength of irradiation the value of the photonic efficiency is almost always lower than the actual quantum yield.

The results of this work, illustrated in Fig. 6, reveal an action spectrum for P25 that has some similarity to that reported by others in the study of the photocatalytic mineralisation of acetic acid, and the diffuse reflectance spectrum of P25, see Figs. 1 and 5, but does not show a good fit at low (<330 nm) wavelengths [3]. The action spectrum (also in Fig. 6) for Kronos VLP 7000 TiO₂ has not, to our knowledge, been reported before and is quite different from the diffuse reflectance spectrum of the Kronos powder (see Fig. 5), in that it reveals little or no visible activity at $\lambda_{\text{excit}} > 400$ nm, and an apparent peak in its activity at ca. 350 nm.

The photonic efficiency values for the photocatalytic degradation of stearic acid both the P25 and Kronos powder films (0.02–0.065) over the wavelength range 380–300 nm are higher than might be initially expected if, as suggested by reaction (1) the disappearance of 1 stearic acid molecule is accompanied by the appearance of 18 molecules of CO₂. In the latter case a maximum photonic efficiency (=quantum yield) of $1/104 = 0.0096$ would be expected, given reaction (1) is a 104 electron transfer process. However, this calculation assumes there are no stable or volatile intermediates formed which, from previous work [6] on stearic acid on P25 films does not appear to be the case, in that during the initial part of the photocatalysed mineralisation of stearic acid on P25 films the amount of CO₂ generated was found to be much less than expected based on reaction (1) [6].

If further work on these, or other semiconductor photocatalyst films, does reveal a photonic efficiency for the photocatalysed reaction (1) of $>1/104$ (or $>\text{unity}$, after correction for the reaction stoichiometry) then a radical chain reaction mechanism is implied. Such a mechanism is not new and has been proposed in, for example, studies of the photocatalytic oxidative mineralisation of acetic acid [4] and acetaldehyde [21]. In a radical chain reaction mechanism the photonic efficiency (once corrected for the overall reaction stoichiometry) can be >1 , with the longer the chain length the greater the photonic efficiency. Further work is required to establish the relationship between the photonic efficiencies for the disappearance of stearic acid, by P25 and Kronos films, as measured here, and the concomitant photonic efficiencies for CO₂ generation, via reaction (1). If values for the latter are found to be $>1/18$, then a radical mechanism appears likely.

3.2. Correction for non-linear dependence of rate upon irradiance

As noted earlier, in general, the kinetics of heterogeneous photocatalysis is found to depend upon irradiance in a non-simple manner. For example, at low irradiances, the initial rate is usually found to be proportional to the irradiance, I , but, dependent upon $I^{1/2}$ at high irradiance. A common interpretation of this effect is that at low I values the overall photocatalytic reaction is dependent directly upon the rate of generation of electron–hole pairs and therefore I , because direct electron–hole pair recombination is a minor process, but at high irradiances, electron–hole pair recombination dominates and the overall rate tends to be dependent upon $I^{1/2}$ [22]. In practice, at the irradiances usually employed in semiconductor photocatalysis (ca. $0.5\text{--}3\text{ mW cm}^{-2}$) it is not uncommon for the rate to be dependent upon I^θ , where $0.5 < \theta < 1$, since, as noted earlier, what constitutes a high or low irradiance value depends upon many factors, including the reaction under study. A nice illustration of the latter is provided by the work of Ohtani et al. [4], who found that even over a range of modest irradiance values

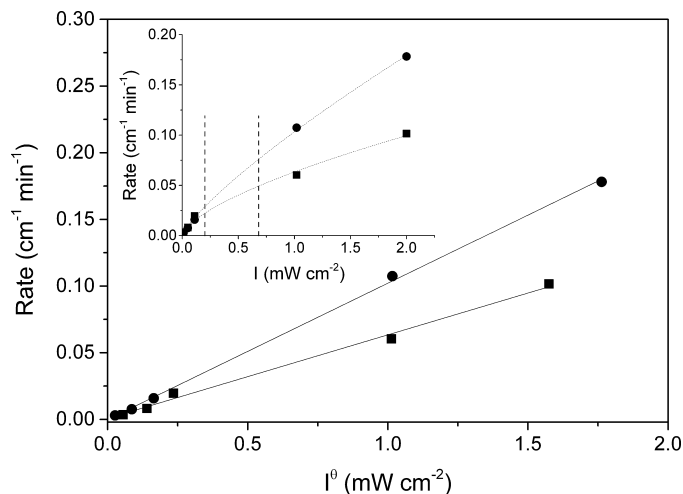


Fig. 7. Inset diagram: plot of measured rate of stearic acid degradation as a function of irradiance for P25 (■) and Kronos (●) films under UVA-light irradiation, using two 8W BLB lamps, with $\lambda_{\text{excit}} = 365$ nm (FWHM ~ 18 nm), a log–log plot of which reveals, $\text{rate} \propto I^\theta$, where $\theta = 0.65$ and 0.82 for P25 and Kronos, respectively. The main diagram is a plot of $\text{rate} \propto I^\theta$, using the data in the inset plot and the values for θ for P25 and Kronos powder films given above. The two broken vertical lines in the inset diagram highlight the range of irradiances (from Fig. 3) used to record the action spectra for P25 and Kronos films.

(e.g. $0.1\text{--}4\text{ mW cm}^{-2}$) the value θ for one photocatalytic reaction, the dehydration of methanol; where $\text{rate} \propto I$, can be very different to that of another, the photomineralisation of acetic acid, where $\text{rate} \propto I^{1/2}$, for mechanistic reasons. Other mechanisms have been proposed for photocatalysis which predict a $\text{rate} \propto I^\theta$ dependence, where $0.5 \leq \theta \leq 1$ [23–25].

For any photocatalytic reaction, the value of θ can be calculated from a study of the photocatalytic rate at different illumination irradiance values, via the slope of the corresponding plot of $\log(\text{initial rate})$ vs. $\log(I)$. In this work, the photocatalytic degradation of stearic acid on the two different film types was studied as a function of irradiance, spanning the range $0.01\text{--}2\text{ mW cm}^{-2}$, using UVA light from a BLB light source. The results of this work are illustrated in Fig. 7 and reveal θ values of 0.65 and 0.82 for films of P25 and Kronos VLP 7000 TiO₂ films, respectively. Assuming, for these two different titania powder films, this dependence of rate (of stearic acid degradation) vs. I holds at all wavelengths covered by the action spectrum, these values for θ can be used to create a modified plot of the action spectra of the two film types, after correction for the non-linear dependence upon irradiance, i.e. a plot of $(\xi' = R_{\text{SA}}/I^\theta)$ vs. λ_{excit} for P25 and Kronos samples of titania. The results are illustrated in Fig. 8, from which it is clear that the action spectrum of P25 tends to level out at shorter wavelengths of irradiation in much the same way its diffuse reflectance spectrum does, as illustrated in Fig. 5. When this modified action spectrum, i.e. ξ' vs. λ_{excit} , is normalised and matched with that of the diffuse reflectance spectrum of P25, the comparison is good, as illustrated by the data in Fig. 1 and suggests that P25 titania is the light-absorbing species in the degradation of stearic acid. The slight blue shift in the onset of photocatalysis (at 390 nm) compared to the diffuse reflectance spectrum (418 nm), could be an indication that the active semiconductor photocatalyst species in driving the photodegradation of SA forward, via reaction (1), is the anatase phase of titania ($E_{\text{bg}} = 3.2\text{ eV}$), rather than its rutile phase (3.0 eV), which is also present in P25 titania. Similar results have been reported elsewhere, in the photocatalytic oxidation of acetic acid, with the anatase phase, in a mixture of anatase and rutile phase, dominating the process and so yielding an action spectrum of pure anatase only [26].

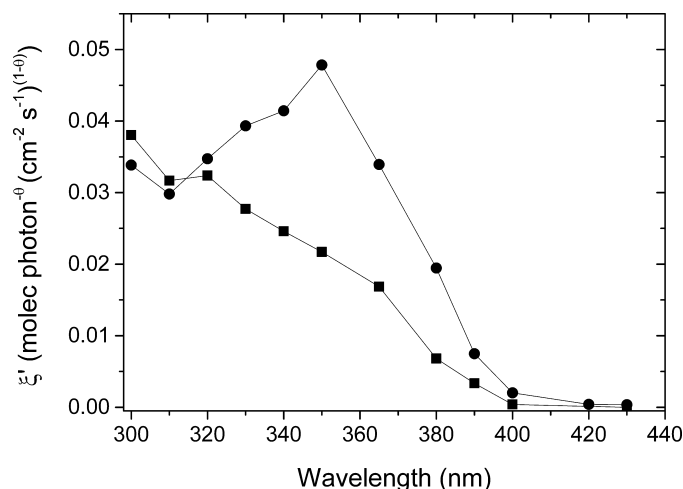


Fig. 8. Modified action spectra plots (i.e. $\xi' = R_{SA}$ (units: molecules of SA degraded $\text{cm}^{-2} \text{s}^{-1}$) / I^0 (units: incident photons $\text{cm}^{-2} \text{s}^{-1}$)), as a function of irradiation wavelength for P25 (■) and Kronos (●) powder films for the photocatalytic degradation of stearic acid; $\theta = 0.65$ and 0.82 for P25 and Kronos, respectively.

The modified action spectrum of Kronos VLP 7000, (Fig. 8) is significantly different from the diffuse reflectance spectrum of the Kronos powder (see Fig. 5), and that of P25 titania, as it exhibits a peak at ca. 350 nm. This result would tend to suggest that the peak might be due to the organic arylcarboxylate photosensitizer, extracted by Kisch et al. [17] from the C-modified titania and identified as the species responsible for its apparent visible light photocatalytic activity, although additional work on photocatalyst stability would seem to argue against this, *vide infra*. Most importantly, given the claims associated with the material, there is little or no evidence of photocatalytic activity (for the degradation of stearic acid) by light of wavelength >400 nm, i.e. no evidence of visible light activity.

3.3. Photocatalyst stability

In the course of this work it was noticed that, after a modest degree of UVA irradiation of the Kronos VLP 7000 TiO_2 powder films in air, with and without a stearic acid coating, they lost most of if not all their initial beige colouration. This loss of colour is rather nicely illustrated by the photograph in Fig. 9, which shows the

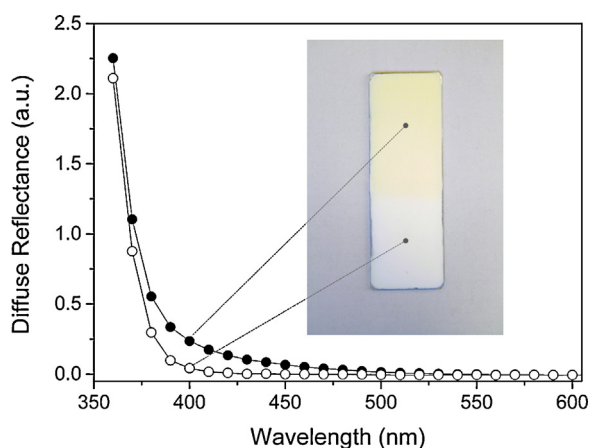


Fig. 9. Kubelka–Munk plots obtained from diffuse reflectance UV/Vis spectra of a typical C-modified TiO_2 Kronos film before (●) and after (○) UVA-light irradiation (3.5 mW cm^{-2}) for 40 min in air. The inset photograph is of a thick Kronos film for which one half of the film was covered (with silver foil) and the other was exposed to the UVA irradiation.

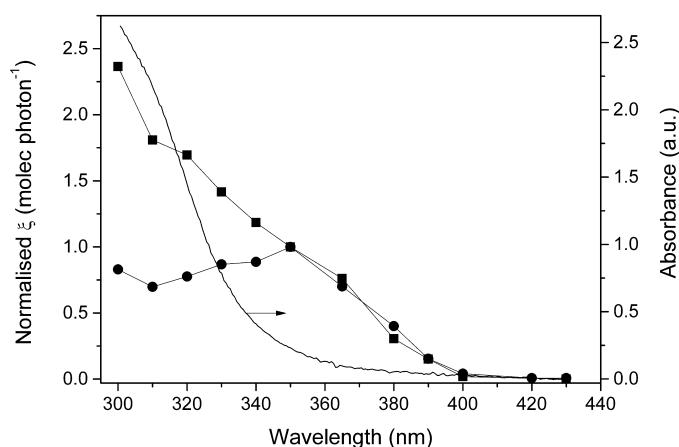


Fig. 10. Normalised action spectra for P25 (■) and Kronos (●) powder films, for the photocatalytic destruction of stearic acid and scaled-up UV/vis absorption spectrum of the UVA-only absorbing species (broken line) extracted from the original Kronos powder using acetonitrile.

photographic results of irradiating (3.5 mW cm^{-2} , BLB lamp) half of a Kronos VLP 7000 TiO_2 powder film in air for 40 min, the other half remaining in the dark. The diffuse reflectance spectra of the irradiated surfaces of the two different halves of the film are also illustrated in Fig. 9 and show quite clearly that the surface of the irradiated part of the film has lost its visible light-absorbing component. Just as importantly, similar results were obtained for the same films using visible light ($21,500 \text{ lx}$) from two 8W Cool white lamps, with and without a UV filter for 60 min irradiation.

The Kronos powder contains a yellow/brown conjugated, organic sensitizer present which has been identified by others as an aryl carboxylate species responsible for its reported photocatalytic visible light activity [17]. This yellow brown species can be extracted from the original Kronos powder using an alkaline aqueous solution [17]. Interestingly, in this work, using acetonitrile as the extraction solvent, the original colouration of the Kronos powder remains unchanged but, an unidentified, UV-absorbing only organic species, with peaks at 284 and 311 nm, is extracted. Other work shows that, unlike the yellow/brown conjugated, organic sensitizer present in the original Kronos powder, this UV-only absorbing species is still present in the photobleached Kronos powder, i.e. compared to the yellow/brown organic species, this UV-absorbing only species is photostable, i.e. more resistant to photodegradation.

The photo-instability of the yellow/brown conjugated, organic sensitizer in the Kronos powder, helps explain the lack of visible activity observed for the Kronos powder films, for the photocatalytic degradation of stearic acid and the similarity in the action spectra of the unbleached and bleached Kronos VLP 7000 TiO_2 powder films, illustrated in Fig. 6, since both features would be expected if the original yellow/brown conjugated, organic sensitizer is substantially photobleached rapidly during the course of the photocatalytic destruction of stearic acid.

When the action spectra of P25 and unbleached Kronos films are normalised (at 350 nm), as illustrated in Fig. 10, there is a clear and striking similarity between the two spectral profiles at wavelengths ≥ 350 nm. In contrast, at wavelengths <350 nm, there is a marked difference between the two, with the photonic efficiency values for Kronos appearing to be noticeably depressed. This observation is consistent with the observation that the original Kronos powder has at least one photostable, UV-only absorbing species, which can be extracted with acetonitrile, and which could act as a UV screen to the titania particles present in Kronos, as illustrated from its UV absorption spectral profile illustrated also in Fig. 10. At

wavelengths above 350 nm, where the UV-only absorbing species does not absorb, both the bleached and unbleached Kronos films have similar action spectra to that of P25 TiO₂, which would be expected if anatase titania is the only absorbing species in all cases.

The above results suggest that Kronos VLP 7000 TiO₂ is not a good example of a commercial, photostable, visible light photocatalyst for the destruction of stearic acid. Indeed, the yellow/brown conjugated, organic sensitizer which has been reported [17] to be responsible for the visible light photocatalytic activity of the Kronos powder appears to lack photostability in terms of resistance to bleaching by either photocatalysis or photosensitisation mechanisms.

4. Conclusions

With films of both P25 and Kronos, the initial rate of photocatalytic destruction of stearic acid, SA, was found to depend upon I^θ , where θ is 0.65 and 0.82 for P25 and Kronos, respectively, at 365 nm. The modified action spectrum of P25 TiO₂ for the photocatalytic destruction of SA appears similar in shape to those reported by others [3] (see Fig. 1) in the photocatalytic destruction of acetic acid and the diffuse reflectance spectrum of P25. The action spectrum of a Kronos VLP 7000 TiO₂ powder film suggests the powder exhibits little or no photocatalytic activity when exposed to light of wavelength >400 nm. The yellow/brown organic species reported to be responsible for the visible light photocatalytic activity of the Kronos powder is readily photobleached in air, upon exposure to a UVA or visible light, with and without a film of stearic acid present. However, the Kronos powder has a relatively photostable, UV-absorbing species which can be extracted using acetonitrile and which may be responsible for the apparent low photonic efficiencies exhibited by the Kronos powder at wavelengths <350 nm, whereas at longer wavelengths the action spectral profiles of P25 and Kronos are very similar, and as expected if anatase titania is the light-absorbing species responsible for the photodegradation of stearic acid. With both powder types the initial rate of photocatalytic destruction of SA was found not to depend directly upon irradiance, but rather to depend upon I^θ , where θ is 0.65 and 0.82 for P25 and Kronos, respectively, at 365 nm.

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